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FINAL REPORT

Infrared Spectroscopy of Simulated
Martian Surface Materials

NASA Ames Grant No. NSG-2277
9/1/77 to 5/30/78

Owen B. Toon/Carl Sagan



Owen B. Toon

Carl Sagan (Principal Investigator)
Laboratory for Planetary Studies
Cornell University
Ithaca, New York 14853

Infrared Spectroscopy of Simulated
Martian Surface Materials

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X-ray fluorescence spectrometry (XRFS) by Viking has determined many of the major elements composing the surface materials on Mars, but does not directly specify the mineralogy of the Martian surface, although it may allow mineralogy to be inferred. Many minerals have characteristic spectral features in the ir (5 to 50 μm). Analyses of Mariner 9 ir transmission spectra of dust in the great 1971 Martian dust storm are informative about mineralogy. Here we compare mineralogy inferred from the Viking XRFS with mineralogy indicated by spectral data. The comparison is done by taking laboratory spectra of Viking analog minerals. We find XRFS and ir data are consistent with clays as the dominant SiO_2 -containing minerals on Mars. The X-ray fluorescence data might also be consistent with the dominance of certain mafic SiO_2 igneous minerals, but the spectral data are probably inconsistent with such materials. Sulfates, inferred by XRFS, are consistent with the spectral data; indeed inferences following Mariner 9 that high- SiO_2 minerals were important on Mars may have been biased by the presence of sulfates. Calcium carbonate, in the quantities indirectly suggested by XRFS ($\sim 7\%$), are inconsistent with the spectral data, but smaller quantities of CaCO_3 are consistent, as are large quantities of other carbonates.

Results

The Viking X-ray fluorescence (XRFS) team directly measured the elemental composition at two sites on the Martian surface. Table I presents the elemental composition, expressed as oxides, for three samples at the Viking 1 lander site (S1, S2, S3), for one sample (U1) at the Viking 2 lander site (Toulmin et al., 1977; Baird et al., 1977) and for two Martian analogs 6041 - (Baird et al., 1977; Toulmin et al., 1977) and B2 - (Baird private communication). Table I shows that the elemental compositions of all the samples at both landing sites are similar as are the elemental compositions of the two terrestrial analogs 6041 and B2. One of the great advantages of XRFS measurements is their sensitivity to minor elemental components such as Ti, K, Cl, Mg, Ca. However, as can be seen by comparing the mineralogy of analog B2 and 6041 in Table I it is not easy to derive useful mineralogical information from the XRFS data. Therefore, it is necessary to supplement XRFS data with other pieces of information.

One valuable, mineralogically sensitive, information source is the infrared measurements made during a Martian dust storm from Mariner 9 by the Infrared Interferometric Spectroscopy (IRIS) experiment. These spectra indicate strong dust absorption near 10 μm and 20 μm . Following the Mariner 9 flights several investigators studied the IRIS dust spectra and concluded that the Martian surface materials could be an igneous rock with an SiO_2 content of $60 \pm 10\%$, or a clay, but the surface could not contain substantial amounts ($< 10\%$) of calcium carbonate (Hanel et al., 1972, Hunt et al., 1973, Toon et al., 1977). By contrast the XRFS results (Table I, and Toulmin et al., 1977) suggest substantial quantities of carbonates are present, that the soil is composed largely of clay minerals or perhaps a low SiO_2 igneous material, and that sulfates are significant minerals.

In order to resolve some of these contradictions we obtained infrared spectra of the Viking B2 and 6041 analogs and of each of their mineralogic constituents. We used a Perkin Elmer 621 spectrometer and suspended the analogs and minerals as dust in CsI pellets. Spectra are shown for the analogs and for orbit 8 of the Mariner 9 spacecraft in Figure 1. Figure 2 illustrates spectra of the minerals composing the B2 analog.

It is clear from Figure 1 that neither 6041 nor B2 is an acceptable analog for the orbit 8 emission spectrum. The B2 analog has two strong bands near 1500 cm^{-1} that are not found in the orbit 8 spectrum. The 6041 analog has only weak bands near 1500 cm^{-1} but the shape of the 1000 cm^{-1} band does not match well with the observations.

An explanation for these problems can be seen in Figure 2. Calcite has a strong band at 1500 cm^{-1} . The large quantity of calcite (CaCO_3) in B2 does not accord with the observations. The second feature in B2 near 1500 cm^{-1} is due to H_2O which is partly in the MgSO_4 and partly in the clays - nontronite and bentonite. Water in clays and sulfates is expected to be seasonably varying on Mars so the discrepancy is not serious. The 6041 analog has two difficulties. Nontronite does not have its 1000 cm^{-1} band well located to agree with the data so the larger quantity of nontronite in 6041 than B2 yields a worse fit for 6041 near 1000 cm^{-1} . In addition 6041 has less MgSO_4 than B-2. Fig. 2 shows MgSO_4 has a strong band at the edge of the 1000 cm^{-1} silicate band, which tends to broaden the 1000 cm^{-1} band. This can also be seen by comparing B2 and B2 minus MgSO_4 in Figure 1 with the orbit 8 data.

These results imply that clay minerals such as those in the B2 analog are consistent with the IRIS observations, but MgSO_4 (or possibly other sulfates) are needed to yield a good fit with the high frequency side of the 1000 cm^{-1} band. The high calcium carbonate content in the B2 mixture is not consistent

with observations. Perhaps other carbonates would be consistent as would lesser quantities of calcite. Adding nontronite to a mixture seems to make the fit to the data worse.

The SO_4 in the Martian surface is probably responsible for the incorrect conclusions following Mariner 9 that the dust was highly siliceous since MgSO_4 tends to broaden the 1000 cm^{-1} band to high frequencies as do highly siliceous minerals. The XRFS data might be consistent with other analogs containing very little SiO_2 . It seems unlikely that these would be consistent with the IRIS data, as, for example, nontronite does not seem a good fit and it has a low frequency 1000 cm^{-1} band as do basic silicates. However, the MgSO_4 complicates the problem and makes qualitative comparisons suspect.

The results presented here can be further quantified by numerical calculations of emission spectra using the optical constants of the minerals (e.g. Toon et al., 1977). Such work is currently underway. We anticipate that this work will quantify the CaCO_3 upper bounds, better consider the significance of MgSO_4 and put limits on magnetite, other possible sulfates and carbonates.

Publications:

The work cited will be submitted for publication in the open literature.

The work has been reported as:

Martian Surface Composition: Comparison of Remote Spectral Studies and In-Situ X-Ray Fluorescence Analysis, O. B. Toon, B. N. Khare, J. B. Pollack, C. Sagan, Ninth Planetary Geology, Principal Investigator Symposium, Tucson, Arizona, 1978.

An abstract of the work has also been submitted for a poster talk at the October 1978 Division of Planetary Sciences Meeting in Los Angeles, Calif.

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Figure Captions

- Figure 1: An emission spectrum taken during orbit 8 of the Mariner 9 Spacecraft is compared with transmission spectra of B2, 6041 and B2 minus MgSO_4 analogs.
- Figure 2: A transmission spectrum of the B2 analog is compared with spectra of the minerals composing the analog.

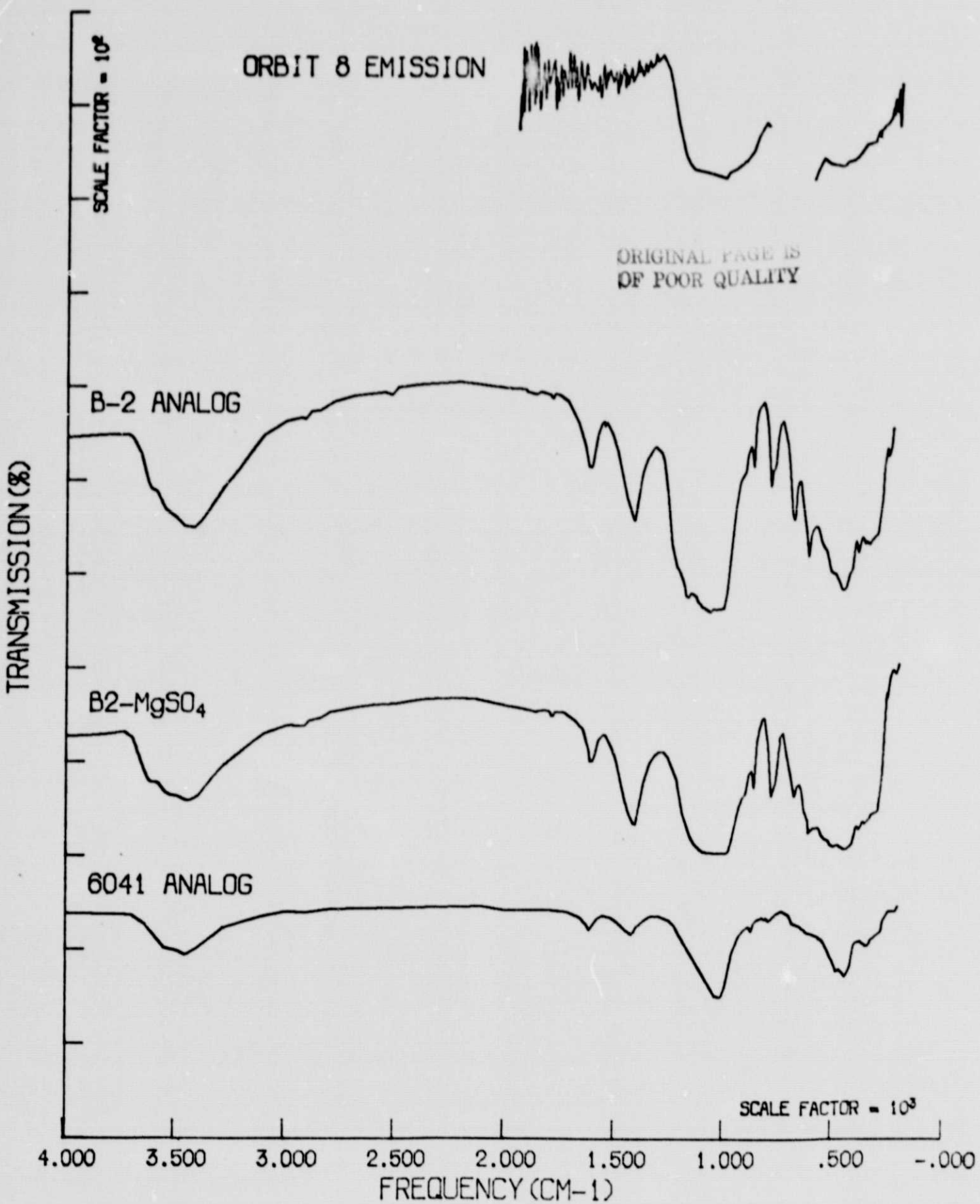
OXIDE COMPOSITION OF MARTIAN SAMPLES AND ANALOGS

	S1	S2	S3	U1	6041	B2
SiO ₂	44.7	44.5	43.9	42.8	44.6	42.2
Al ₂ O ₃	5.7	----	5.5	----	5.5	5.9
Fe ₂ O ₃	18.2	18.0	18.7	20.3	18.6	17.0
MgO	8.3	----	8.6	----	5.4	7.0
CaO	5.6	5.3	5.6	5.0	6.0	5.7
K ₂ O	< 0.3	< 0.3	< 0.3	< 0.3	.12	0.2
TiO ₂	0.9	0.9	0.9	1.0	0.8	1.1
SO ₃	7.7	9.5	9.5	6.5	8.4	12.3
Cl	0.7	0.8	0.9	0.6	0.5	0.5

MINERAL COMPOSITION OF MARTIAN ANALOGS

	6041	B2
Nontronite	49.5	17.5
Bentonite	18.2	29.8
Kieserite	13.7	18.5
Quartz	7.5	14.4
Calcite	4.9	7.0
Hematite	2.5	---
Magnetite	2.4	---
Maghemite	---	11.1
Halite	0.8	0.8
Rutile	---	1.0

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